

PHENOXYALUMINIUM COMPOUNDS

III*. COMPLEXES OF PHENOXYALUMINIUM COMPOUNDS WITH BENZONITRILE

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Summary

The complexing abilities of seventeen monophenoxyaluminium compounds with benzonitrile were investigated. It was revealed that most of them form complexes in equilibrium with substrates. Only $(\text{PhO})\text{AlX}_2$ [$\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{PhO} = \text{phenoxy-}$, and substituted phenoxy-, ($s\text{-PhO}$)] form stoichiometric complexes, and $\text{R}_2\text{Al}(\text{OPh})$ and $\text{Me}_2\text{Al}(s\text{-PhO})$ are inactive towards benzonitrile.

From these results the basicity of bridging oxygen is shown to be much higher in $\text{R}_2\text{Al}(\text{OPh})$ than in $(\text{PhO})\text{AlX}_2$. The donor-acceptor interaction between aluminium and its substituents is discussed.

Introduction

Previous papers in the series dealt with the synthesis and structure of monophenoxyaluminium compounds [1,2]. The complexing abilities of these compounds with organic donor molecules, and their acidities were of great interest. Many organoaluminium complexes have already been investigated and it has been stated that most of these form stable 1/1 stoichiometric complexes.

It was only by formation of complexes with weak donor molecules, e.g. some etherates of organoaluminium compounds, that the existence of an equilibrium between the products and their substrates was established [3]. A higher ratio of donor to organoaluminium compound in complexes when very strong donors are used is postulated by Wallbridge [4,5] and Smith [6]. The donor abilities of bases complexed with organoaluminium compounds [4,7 - 9] and the acidity of these acceptors [10 - 12] has also been of interest.

Result and discussion

1. Basicity of substituents and equilibrium of complex formation

An attempt was made at forming the complex of benzonitrile with

*For part I see ref. 1, for Part II see ref. 2.

TABLE 1

C≡N STRETCHING FREQUENCIES^a (CM⁻¹) OF BENZONITRILE COMPLEXED WITH PHENOXY- AND 2,6-DIMETHYLPHENOXYALUMINIUM COMPOUNDS
Molar ratio 1/1, 3% benzene solution, $\nu(\text{C}\equiv\text{N})_f$ in benzene solution, 2233 cm⁻¹

Compound	$\nu(\text{C}\equiv\text{N})_f$	$\nu(\text{C}\equiv\text{N})_c$	$\Delta\nu(\text{C}\equiv\text{N})$	
1	Me(PhO)AlCl	2233 m	2289 s	+56
2	Et(PhO)AlCl	2233 m	2290 s	+57
3	Et(PhO)AlF	2233 s	2290 m	+57
4	Me(PhO)AlBr	2233 m	2286 s	+53
5	Et(PhO)AlBr	2233 m	2289 s	+56
6	Me(PhO)AlI	2233 w	2280 s	+47
7	Et(PhO)AlI	2233 w	2281 s	+48
8	(PhO)AlCl ₂		2288 vs	+55
9	Et ₂ Al(DMP)	2233 s	2277 m	+44
10	Me(DMP)AlCl		2285 s	+52
11	Me(DMP)AlBr	2233 m	2283 s	+50
12	Me(DMP)AlI	2233 vw	2277 s	+44
13	(DMP)AlCl ₂		2280 s	+53 ^b
14	(DMP)AlBr ₂		2283 vs	+50
15	Me(MeO)AlCl	2233 m	2284 s	+51

^aIn the IR spectra of complexes of Me₂AlOPh, Et₂AlOPh and Me₂Al(DMP) with benzonitrile in the region 2200 - 2300 cm⁻¹ only $\nu(\text{C}\equiv\text{N})_f$ is present. ^bComplex is scarcely soluble in benzene; spectrum in nujol mull [$\nu(\text{C}\equiv\text{N})_f$ 2227 cm⁻¹].

R_n(RO)AlX_{2-n} (n = 0,1,2; R = Me, Et; RO = PhO, 2,6-dimethylphenoxy-(DMP) and MeO, and X = F, Cl, Br, I).

Benzonitrile was used as the donor molecule because it has the advantage of having reasonable donor properties and very low steric hindrance.

The results are presented in Table 1. Only uncomplexed compounds were present in solutions of Me₂AlOPh, Et₂AlOPh and Me₂Al(DMP) in benzonitrile since only $\nu(\text{C}\equiv\text{N})_f$ is observed* in the C≡N stretching region. Stable crystalline complexes are formed when benzonitrile and Me(DMP)AlX are mixed together in molar ratio 1/1. These complexes all form bridges through the halogen substituents which are much weaker electron donors than the nitrogen atom in benzonitrile. (PhO)AlCl₂ also forms a stable complex with benzonitrile [$\nu(\text{C}\equiv\text{N})_f$ in 1/1 mixtures of these compounds disappears].

Table 1 shows that some of the compounds investigated, when mixed with benzonitrile in molar ratio 1/1, exhibit spectra containing two C≡N stretching vibrations, one due to free, and the other to complexed benzonitrile. This indicates an equilibrium between substrate and product in the complexation reaction. The following observations support this supposition.

(i). To the 1/1 complex of dimethylaluminium chloride with benzonitrile [$\nu(\text{C}\equiv\text{N})_c$ 2279 cm⁻¹] in benzene, was added a solution of phenol (1 mole/mole of complex). In the IR spectra of the reaction products the band at 2279 cm⁻¹ was absent and two new bands had formed which correspond to the (C≡N) bands of free benzonitrile (2233 cm⁻¹), and benzonitrile complexed to Me(PhO)AlCl (2289 cm⁻¹).

(ii) The intensity ratios of $\nu(\text{C}\equiv\text{N})_f$ and $\nu(\text{C}\equiv\text{N})_c$ were investigated for different molar ratios of benzonitrile and Me(PhO)AlCl (see Fig. 1). It can be

* $\nu(\text{C}\equiv\text{N})_f$ is the stretching frequency of the free C≡N bond. $\nu(\text{C}\equiv\text{N})_c$ is the stretching frequency of the complexed C≡N bond.

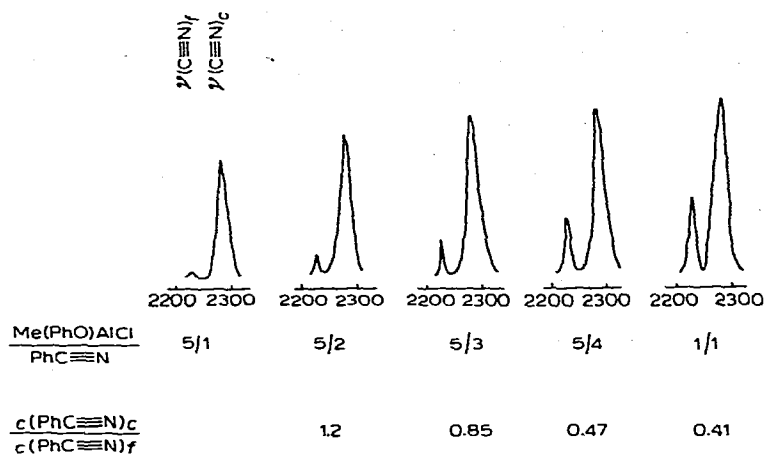
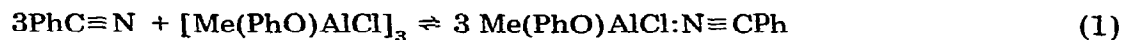


Fig. 1. The $\nu(\text{C}\equiv\text{N})$ region of the IR spectrum of $\text{Me}(\text{PhO})\text{AlCl}\cdot\text{benzonitrile}$ at different molar ratios of the reagents. The concentration of complexed and uncomplexed organoaluminium in benzene remains constant.

seen* from Fig. 1 that the intensities of both bands increased with the amount of benzonitrile added. This is good evidence for an equilibrium.

From a plot of intensity vs. concentration, the molar extinction of the $\nu(\text{C}\equiv\text{N})_f$ band was obtained. Using this value the concentration of free and complexed benzonitrile was calculated for different ratios of the reagents. The molar ratios of benzonitrile, both complexed and free, are given in Fig. 1.

For the complexation reaction proposed (eqn. 1) the equilibrium constant was calculated:



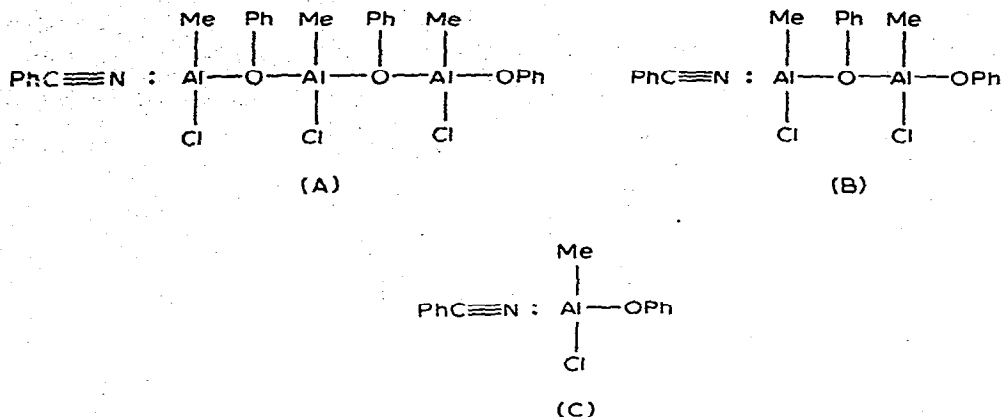
$$K = C_c^3 / (C_d^3 \cdot C_{\text{OAC}})$$

where C_c is the concentration of complex, C_{OAC} is the concentration of trimer $[\text{Me}(\text{PhO})\text{AlCl}]_3$ and C_d is the concentration of donor.

The values of K decreased markedly with increasing ratio of benzonitrile to $\text{Me}(\text{PhO})\text{AlCl}$. This suggests that other complexes may be formed. There is no further evidence for the presence of other complexes but the authors suggest that in the mixture of benzonitrile and phenoxyaluminium compounds there is an equilibrium of benzonitrile and compounds (A), (B) and (C).

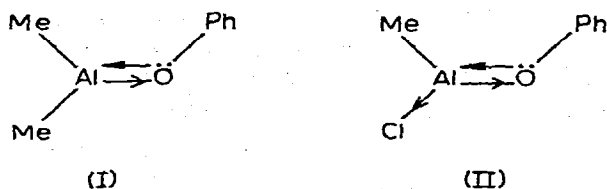
In the complexation reaction competition occurs between the electron donor properties of the bridging atom and those of the donor atom of the base used (benzonitrile). Equilibrium (1) occurs when the basicities of both donor atoms are similar, e.g. of the nitrogen atom in $\text{PhC}\equiv\text{N}$ and the oxygen atom in $\text{Me}(\text{PhO})\text{AlCl}$. When a bridging atom is obviously less basic than the donor atom of the base used stoichiometric complexes are formed, e.g. $\text{Me}(\text{DMP})\text{AlCl}$ — which is associated through its chlorine atoms — forms a 1/1 complex with PhCN . Conversely when the bridging atoms are very strongly basic compared with the donor atom of the added base no reaction takes place, e.g., Me_2AlOPh and $\text{Me}_2\text{Al}(\text{DMP})$ do not form complexes with benzonitrile. The different ef-

* The intensity of the $\nu(\text{C}\equiv\text{N})_f$ band is lower than of the $\nu(\text{C}\equiv\text{N})_c$ band but although the first band is the weaker the concentration of free benzonitrile is considerable.



fective basicity of oxygen in phenoxy- and 2,6-dimethylphenoxy- substituents in different aluminium compounds is caused mainly by the electronegativity of the aluminium atom in the compounds studied, and by steric hindrance.

(a). *Electronegativity.* Structures (I) and (II) show how replacing the methyl group by a chlorine atom increases the electronegativity of aluminium. This change is accompanied by an increased shift of the electrons on the



oxygen atom back to the aluminium atom. Such an action decreases the electron density on the oxygen and causes lowering of its basicity, which in compound (II) may be compared with that of nitrogen in benzonitrile. In $\text{Me}_2\text{Al}(\text{OPh})$, (I), there is less interaction between aluminium and the oxygen electrons. In this case the oxygen has stronger donor properties than benzonitrile and a complex is therefore not formed.

(b). *Steric hindrance.* The donor ability of the oxygen atom of the DMP group is at least as great as that of the phenoxy group, but the oxygen of DMP is hindered by methyl groups which cause the effective basicity of the oxygen atom to be lower than that of a halogen atom. This is apparent in the formation of halogen-bonded dimers, e.g. $\text{Me}(\text{DMP})\text{AlX}$. When bulkier groups are bonded to the aluminium atom, e.g. ethyl rather than methyl in $\text{R}_2\text{Al}(\text{DMP})$, weaker oxygen bridging bonds are formed, the oxygen having an effective donor ability only comparable to that of nitrogen in benzonitrile. Thus, $\text{Et}_2\text{Al}(\text{DMP})$ forms a complex with PhCN which is in equilibrium with the substrates, with the equilibrium being shifted towards the substrates.

II. Acidity of monophenoxyaluminium compounds

The shifts of the $\text{C}\equiv\text{N}$ band in complexes of benzonitrile with monophenoxyaluminium compounds are listed in Table 1. The phenoxy group is a stronger acceptor group than DMP in the same compound, e.g. in Nos. 1 and 10, or 4 and 11.

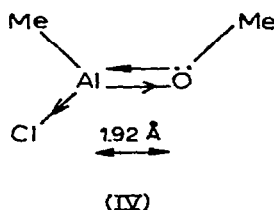
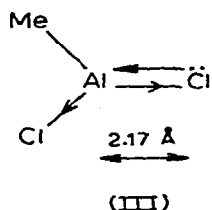
The halogen substituents, except iodine, cause nearly the same acidity of aluminium in the same phenoxyaluminium compounds:

For $\text{Et}(\text{PhO})\text{AlX}$: X, $\Delta\nu(\text{cm}^{-1})$; F, 57; Cl, 57; Br, 56; I, 48.

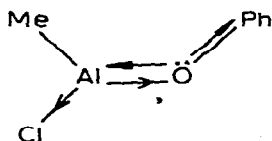
The replacement of methyl by ethyl causes a slight increase of $\Delta\nu$ which has been observed previously [10]. The electron acceptor property of the phenoxy group is greater than that of the chloride substituent (for the complex of PhCN and MeAlCl_2 $\Delta\nu(\text{C}\equiv\text{N})$ is 51 cm^{-1} but for $\text{Me}(\text{PhO})\text{AlCl}$ it rises to 56 cm^{-1}).

Electron releasing substituents on oxygen, e.g. methyl as opposed to phenyl, decrease the acceptor ability of the oxygen. Complexes of $\text{Me}(\text{MeO})\text{AlCl}$ and of MeAlCl_2 with benzonitrile caused the same shift of the $\text{C}\equiv\text{N}$ band. This indicated that both MeO and Cl substituents have the same influence on the aluminium atom in these compounds.

The greater electronegativity of oxygen as compared to chlorine would imply that $\text{Me}(\text{MeO})\text{AlCl}$ should be a stronger electron acceptor than MeAlCl_2 ,



but the stronger electron accepting aluminium atom interacts more effectively with the electrons of the substituent on oxygen. The shorter the bond the stronger is this "back electron donation" towards the aluminium atom*. Since the covalent radius of oxygen is smaller than that of chlorine, and methyl is an electron-releasing group, the "back electron donation" is larger for oxygen (IV), than for chlorine (III). The p_π conjugation of the phenoxy group diminishes the possibility of oxygen to aluminium "back electron donation" and as a result the electronegativity of aluminium increases. (E.g. Table 1, Nos. 1 and 15.)



Experimental

The phenoxy- and 2,6-dimethylphenoxyaluminium compounds were obtained according to procedures described earlier [1,2]. Benzonitrile (Xenon, Łódź) was distilled and dried using 4 Å molecular sieves.

Preparation of complexes

To standard solutions of the monophenoxyaluminium compounds in

*Bond lengths in structures (III) and (IV) are the sum of the covalent radii and are larger than those determined by X ray methods. For further details on bond lengths in organoaluminium compounds see ref. 13.

benzene was slowly added a standard solution of benzonitrile in benzene until the molar ratio was 1/1. 1/1 Complexes of $\text{Me}(\text{DMP})\text{AlCl}$ and $(\text{DMP})\text{AlCl}_2$ with benzonitrile precipitated as yellowish white solids. (Analyses: found: Al, 8.8; Cl, 11.3. $\text{Me}(\text{DMP})\text{AlCl}\cdot\text{PhC}\equiv\text{N}$ calcd.: Al, 8.96; Cl, 11.75%. Found: Al, 8.2; Cl, 21.0. $(\text{DMP})\text{AlCl}_2\cdot\text{PhC}\equiv\text{N}$ calcd.: Al, 8.39; Cl, 22.1%.)

IR spectra were recorded in the range $2200 - 2300 \text{ cm}^{-1}$ on a Zeiss UR 10 spectrometer on 3% solutions in benzene in a sample cell of path length 0.12 mm.

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